The DBDS Corrosive Sulphur Formation Problem and Its Implications.

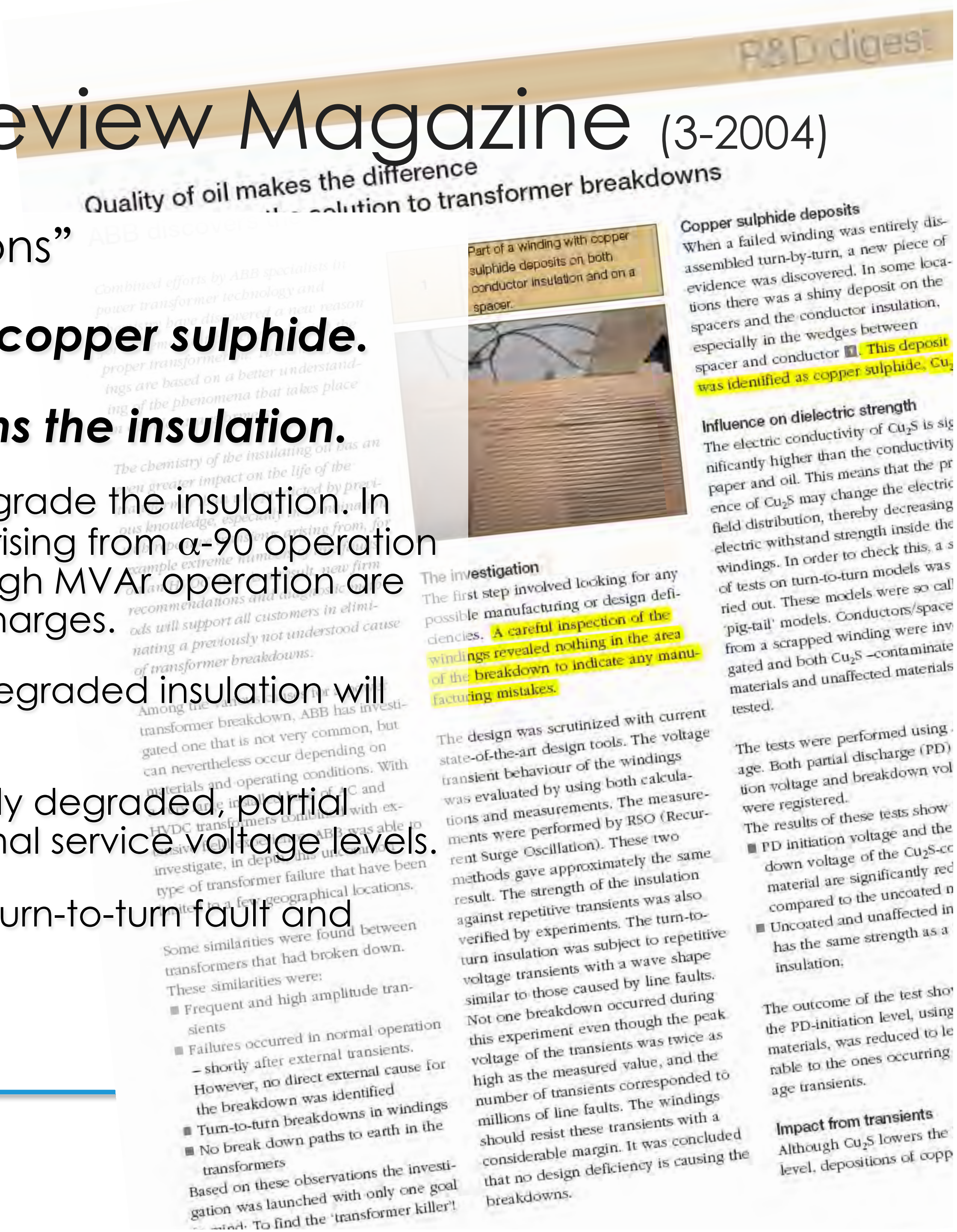
History and TWO important projects

CONCLUSIONS.

INDEPENDENT DIAGNOSTIC SERVICES
VPdiagnose
SWEDEN
NORWAY FINLAND

Lars Arvidsson
General Manager,
Master of Science **Chemical Process Engineering**
Lund University of Technology 1979
VPdiagnose *Västerås Sweden*

A Technical Review Magazine (3-2004)



R&D digest

Quality of oil makes the difference

ABB discovers the solution to transformer breakdowns

Combined efforts by ABB specialists in power transformer technology and [illegible] have discovered a new reason [illegible] proper transformer oil. [illegible] ings are based on a better understanding of the phenomena that takes place [illegible]

The chemistry of the insulating oil has an [illegible] greater impact on the life of the [illegible] recommendations [illegible] ods will support all customers in eliminating a previously not understood cause of transformer breakdowns.

Among the various causes for a [illegible] transformer breakdown, ABB has investigated one that is not very common, but can nevertheless occur depending on materials and operating conditions. With [illegible] of AC and HVDC transformers combined with extensive field experience, ABB was able to investigate, in depth, this uncommon type of transformer failure that have been limited to a few geographical locations.

Some similarities were found between transformers that had broken down. These similarities were:

- Frequent and high amplitude transients
- Failures occurred in normal operation – shortly after external transients. However, no direct external cause for the breakdown was identified
- Turn-to-turn breakdowns in windings
- No break down paths to earth in the transformers

Based on these observations the investigation was launched with only one goal in mind: To find the 'transformer killer'!

Part of a winding with copper sulphide deposits on both conductor insulation and on a spacer.

The investigation

The first step involved looking for any possible manufacturing or design deficiencies. A careful inspection of the windings revealed nothing in the area of the breakdown to indicate any manufacturing mistakes.

The design was scrutinized with current state-of-the-art design tools. The voltage transient behaviour of the windings was evaluated by using both calculations and measurements. The measurements were performed by RSO (Recurrent Surge Oscillation). These two methods gave approximately the same result. The strength of the insulation against repetitive transients was also verified by experiments. The turn-to-turn insulation was subject to repetitive voltage transients with a wave shape similar to those caused by line faults. Not one breakdown occurred during this experiment even though the peak voltage of the transients was twice as high as the measured value, and the number of transients corresponded to millions of line faults. The windings should resist these transients with a considerable margin. It was concluded that no design deficiency is causing the breakdowns.

Copper sulphide deposits

When a failed winding was entirely disassembled turn-by-turn, a new piece of evidence was discovered. In some locations there was a shiny deposit on the spacers and the conductor insulation, especially in the wedges between spacer and conductor ■. This deposit was identified as copper sulphide, Cu

Influence on dielectric strength

The electric conductivity of Cu_2S is sig nificantly higher than the conductivity paper and oil. This means that the pr ence of Cu_2S may change the electric field distribution, thereby decreasing electric withstand strength inside the windings. In order to check this, a s of tests on turn-to-turn models was ried out. These models were so call 'pig-tail' models. Conductors/space from a scrapped winding were inv gated and both Cu_2S –contaminate materials and unaffected materials tested.

The tests were performed using age. Both partial discharge (PD) tion voltage and breakdown vol were registered.

The results of these tests show

- PD initiation voltage and the down voltage of the Cu_2S-co material are significantly red compared to the uncoated n
- Uncoated and unaffected in has the same strength as a insulation.

The outcome of the test sho the PD-initiation level, using materials, was reduced to le rable to the ones occurring age transients.

Impact from transients

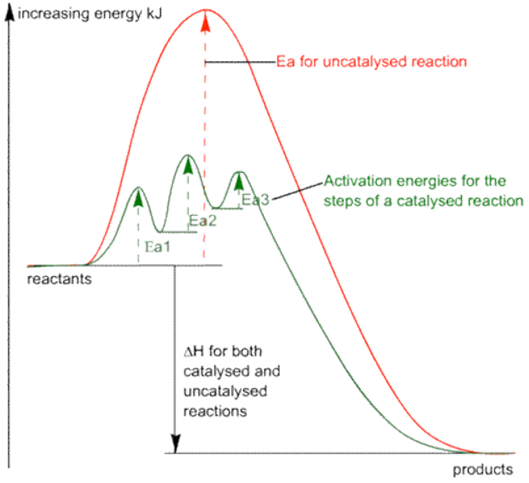
Although Cu_2S lowers the level, depositions of copp

"Brief summary of conclusions"

- ***Aggressive oil produces copper sulphide.***
- ***Copper sulphide weakens the insulation.***
- Repetitive transients further degrade the insulation. In the case of HVDC, transients arising from α-90 operation or transients from continuous high MVAr operation are sufficient to initiate partial discharges.
- A partial discharge PD in the degraded insulation will not extinguish.
- When the insulation is sufficiently degraded, partial discharge will continue at normal service voltage levels.
- A partial discharge leads to a turn-to-turn fault and transformer breakdown."

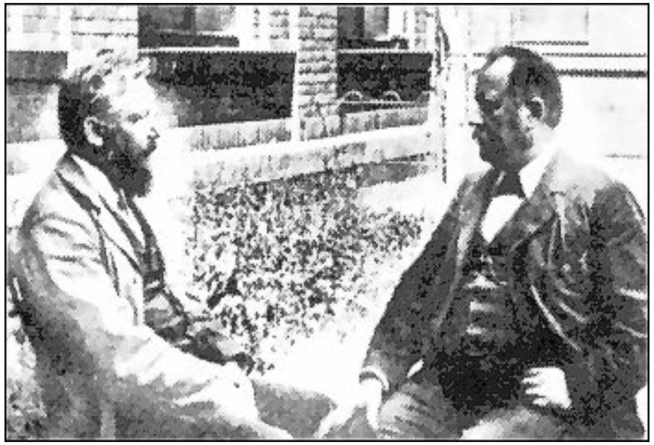
THE ARRHENIUS EQUATION (1889)

$$\delta[C]/\delta t = A * e^{(-\Delta E_a/RT)}$$


increasing energy kJ
Ea for uncatalysed reaction
Activation energies for the steps of a catalysed reaction
Ea1
Ea2
Ea3
reactants
ΔH for both catalysed and uncatalysed reactions
products

States the chemical reaction rate dependence on

- ✓*Absolute temperature T (K)*
- ✓*Activation Energy* (ΔE_a)

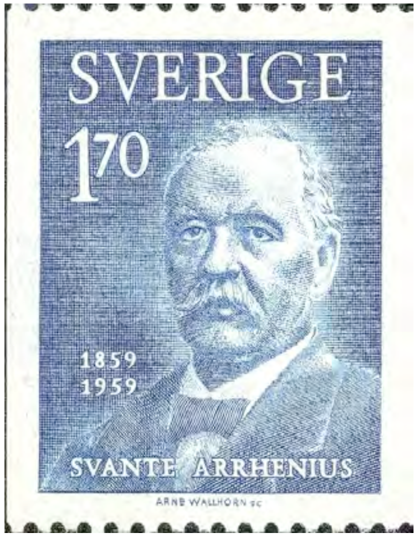


Svante Arrhenius
Nobel Laureate 1903

Development of the

" Theory of Electrolytic Dissociation"

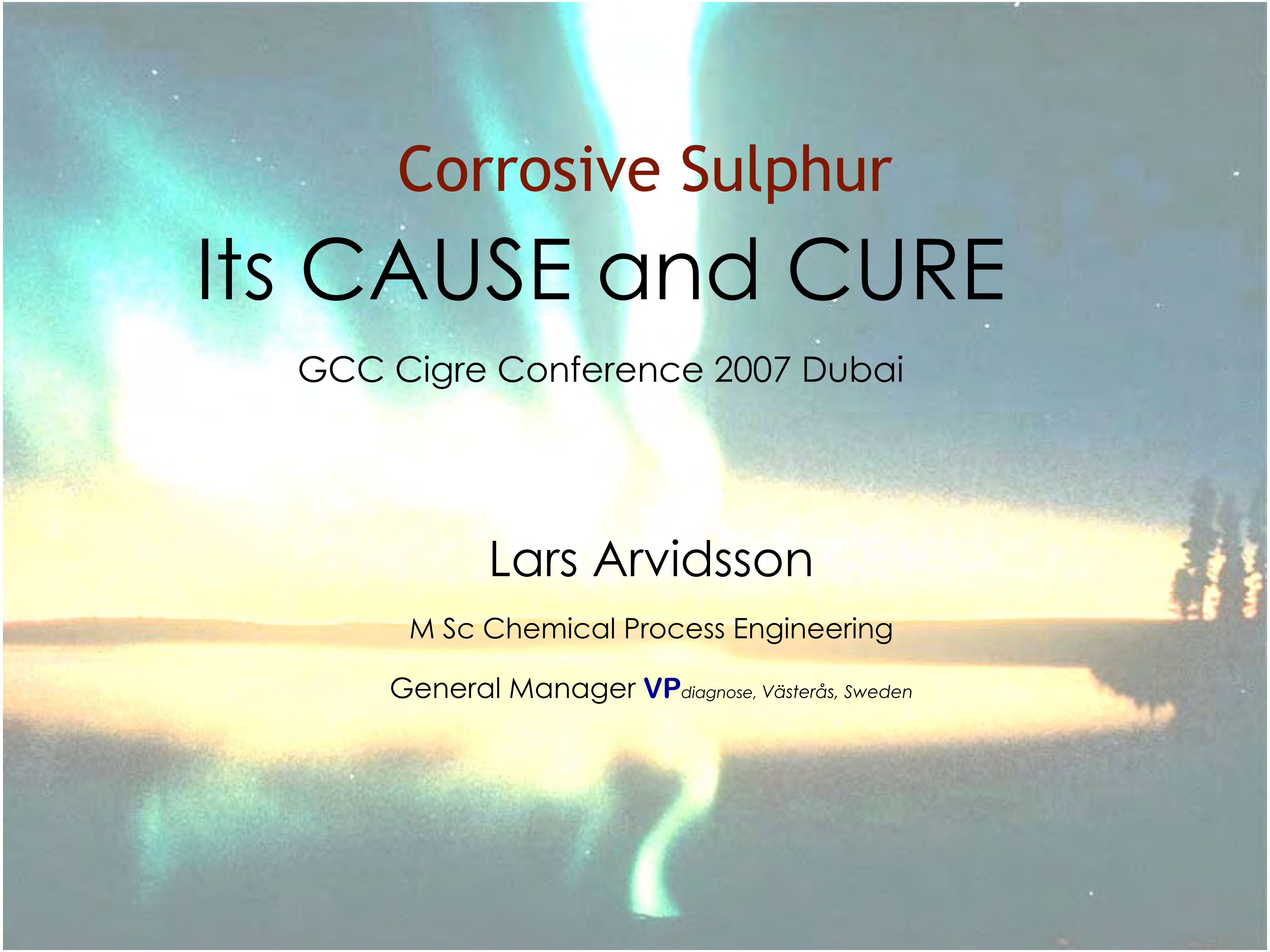
Coined "**Greenhouse Effect**" in 1896. (Verified in 1987)



Why Not Solve the Problem when ARRHENIUS Equation gives the ANSWER ?

- Corrosive Sulphur = **ACTIVE** Sulphur.
- **ACTIVE** Sulphur used in Lubrication for almost a Century.

Utilizing the Temperature Selectivity Obtained by Choosing Different Organic Sulphur Containing Molecules.



Corrosive Sulphur
Its CAUSE and CURE

GCC Cigre Conference 2007 Dubai

Lars Arvidsson

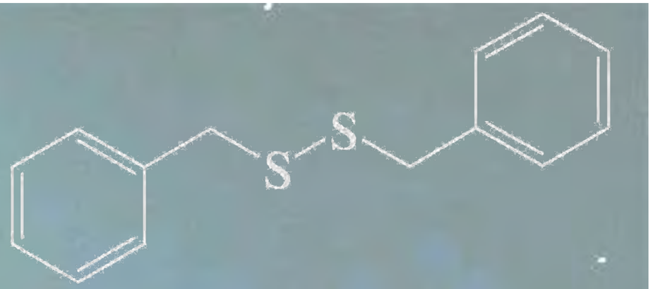
M Sc Chemical Process Engineering

General Manager **VP***diagnose, Västerås, Sweden*

Potentially Corrosive ADDITIVE **DBDS** Discovered

- Fabio Scattigio et al. of Terna Italy found DBDS in the Oil (2006).
- Its presence in the oil was the common factor for a series of 120 reactors which failed at a rate of 20 per annum.

What is Required?

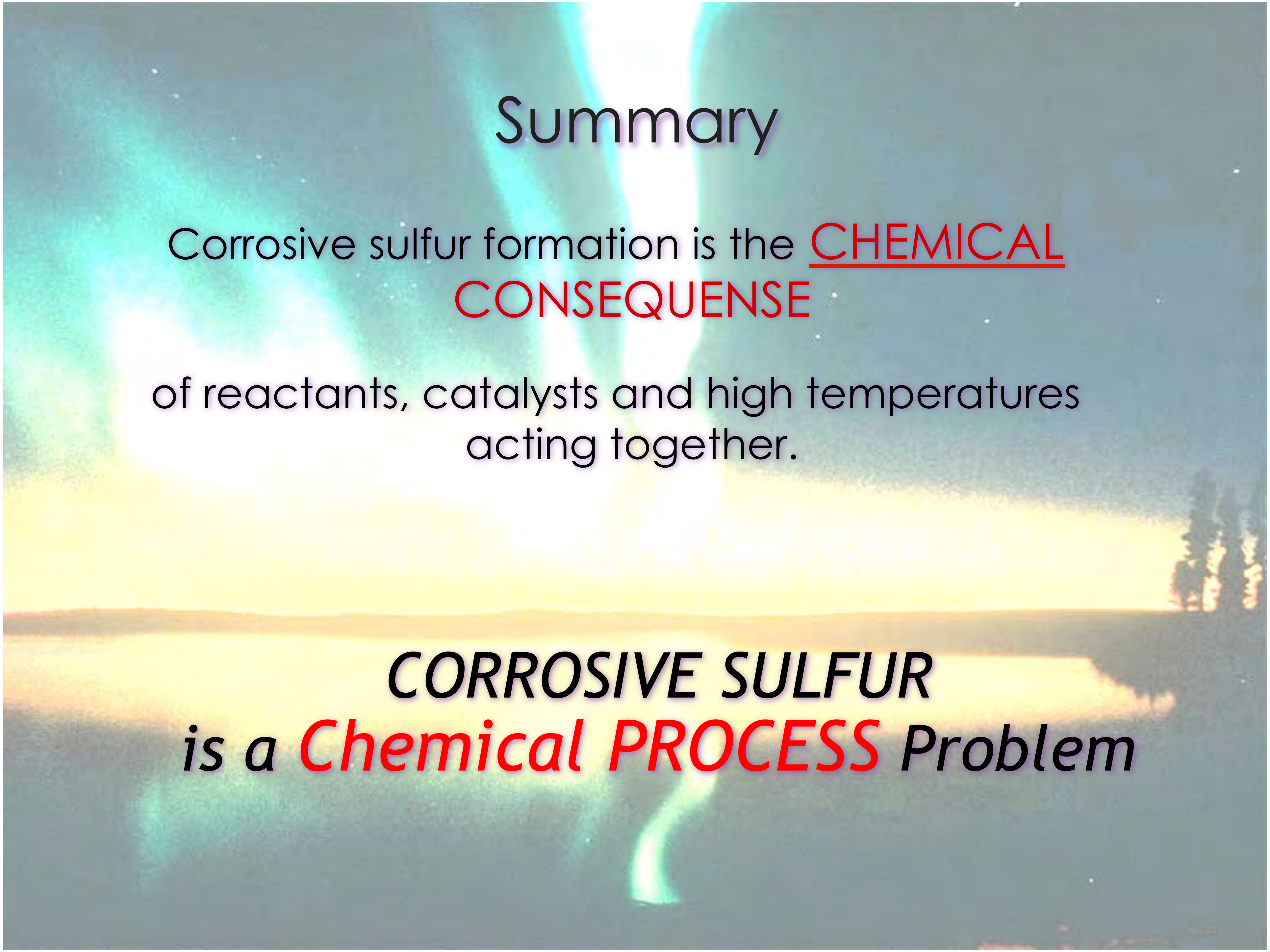


Dibenzyl disulfide

- Sulfur containing, chemically ACTIVE compounds!
- Catalytically ACTIVE surfaces!
- High Temperature!
- TIME

Not Enamelled Copper windings

Modern Transformer Operating Conditions

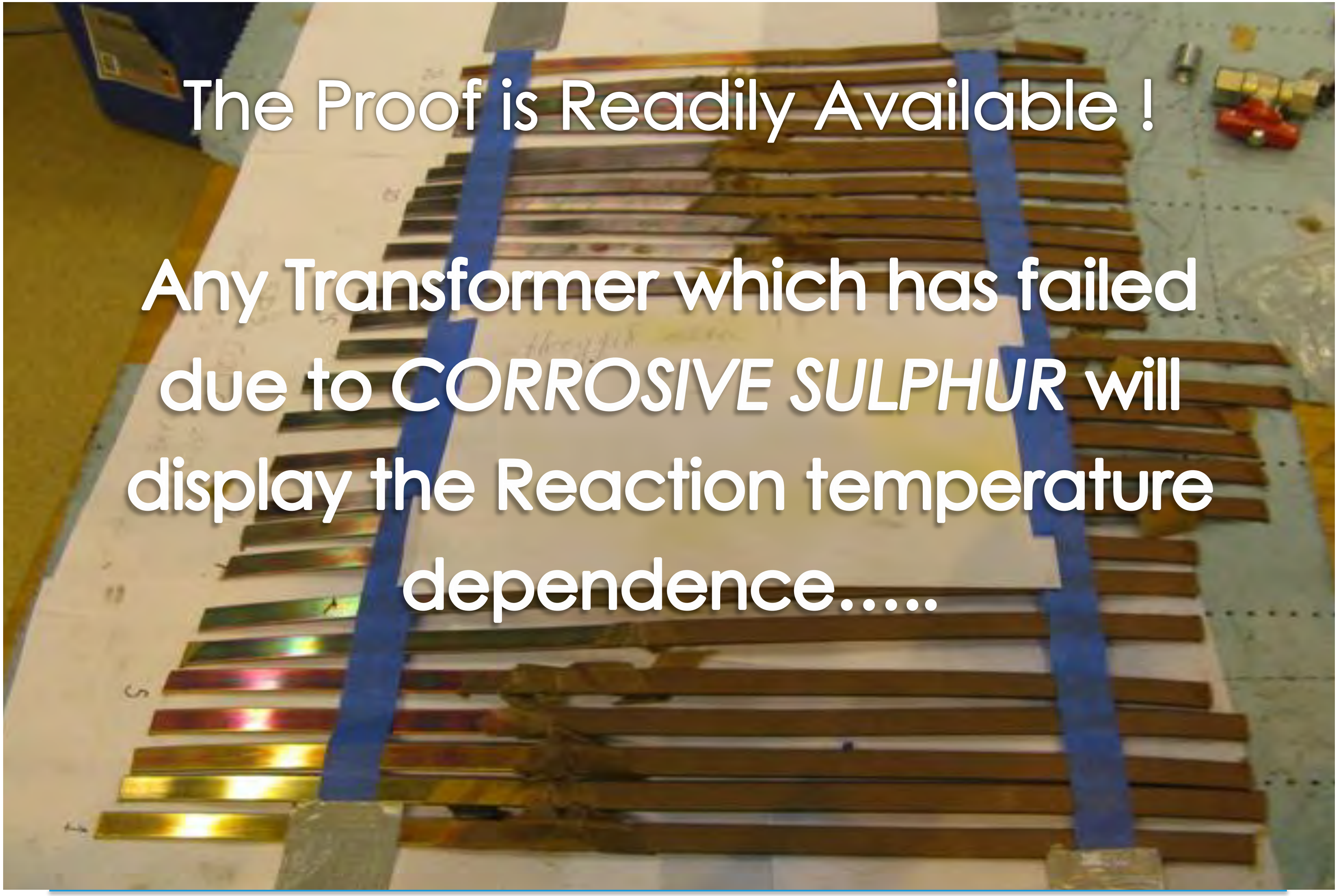


Summary

Corrosive sulfur formation is the CHEMICAL CONSEQUENSE

of reactants, catalysts and high temperatures acting together.

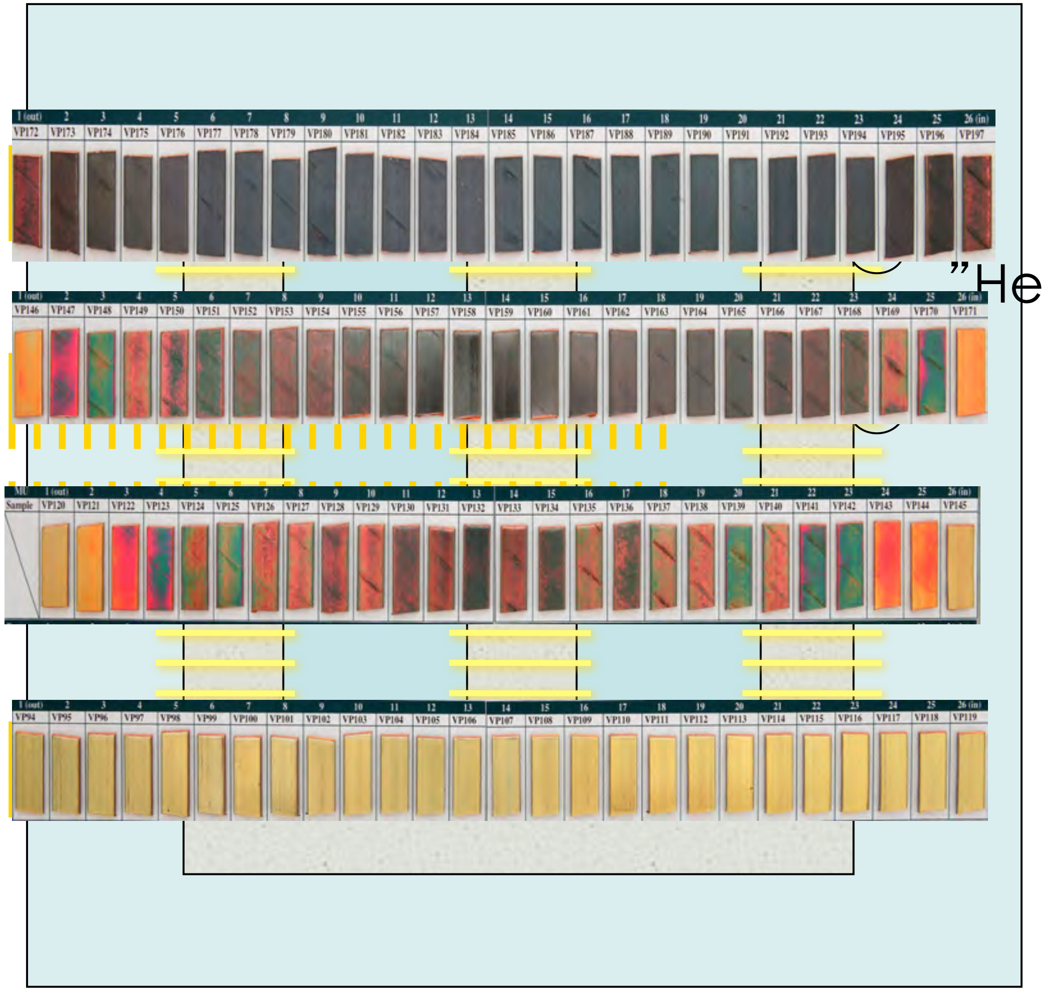
CORROSIVE SULFUR
is a Chemical PROCESS Problem

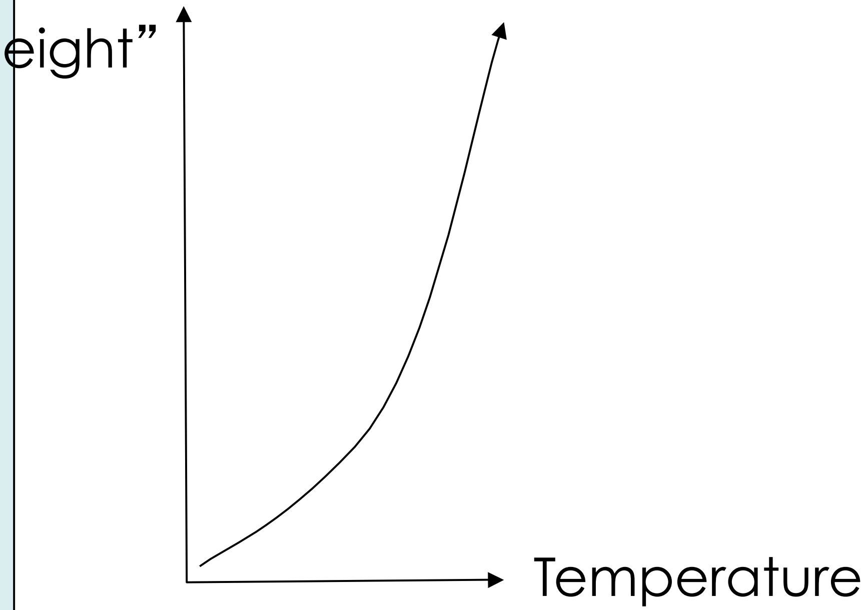


The Proof is Readily Available !

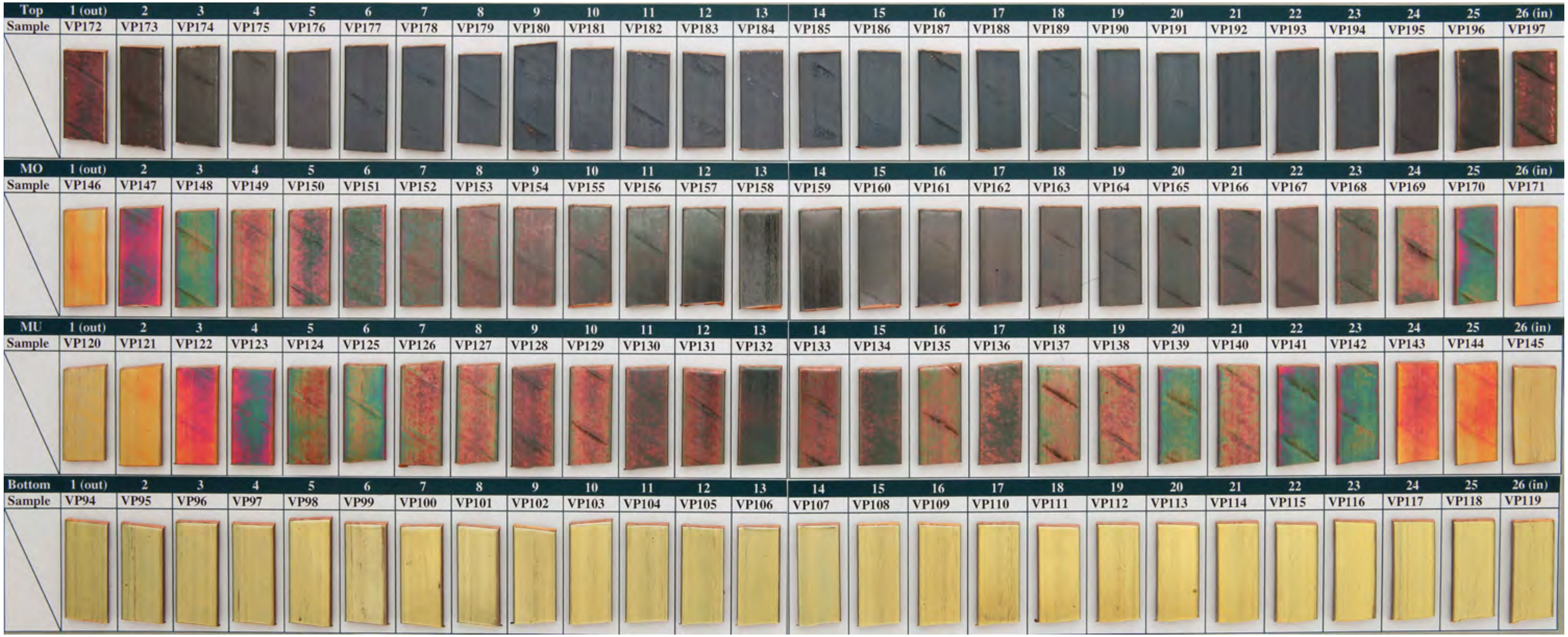
Any Transformer which has failed due to *CORROSIVE SULPHUR* will display the Reaction temperature dependence.....

SULTARTANGI SP2 Iceland


1 (out) 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 (in)
VP172 VP173 VP174 VP175 VP176 VP177 VP178 VP179 VP180 VP181 VP182 VP183 VP184 VP185 VP186 VP187 VP188 VP189 VP190 VP191 VP192 VP193 VP194 VP195 VP196 VP197
1 (out) 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 (in)
VP146 VP147 VP148 VP149 VP150 VP151 VP152 VP153 VP154 VP155 VP156 VP157 VP158 VP159 VP160 VP161 VP162 VP163 VP164 VP165 VP166 VP167 VP168 VP169 VP170 VP171
MU 1 (out) 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 (in)
Sample VP120 VP121 VP122 VP123 VP124 VP125 VP126 VP127 VP128 VP129 VP130 VP131 VP132 VP133 VP134 VP135 VP136 VP137 VP138 VP139 VP140 VP141 VP142 VP143 VP144 VP145
1 (out) 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 (in)
VP94 VP95 VP96 VP97 VP98 VP99 VP100 VP101 VP102 VP103 VP104 VP105 VP106 VP107 VP108 VP109 VP110 VP111 VP112 VP113 VP114 VP115 VP116 VP117 VP118 VP119



SULTARTANGI SP2 Iceland



Top	1 (out)	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26 (in)
Sample	VP172	VP173	VP174	VP175	VP176	VP177	VP178	VP179	VP180	VP181	VP182	VP183	VP184	VP185	VP186	VP187	VP188	VP189	VP190	VP191	VP192	VP193	VP194	VP195	VP196	VP197
MO	1 (out)	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26 (in)
Sample	VP146	VP147	VP148	VP149	VP150	VP151	VP152	VP153	VP154	VP155	VP156	VP157	VP158	VP159	VP160	VP161	VP162	VP163	VP164	VP165	VP166	VP167	VP168	VP169	VP170	VP171
MU	1 (out)	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26 (in)
Sample	VP120	VP121	VP122	VP123	VP124	VP125	VP126	VP127	VP128	VP129	VP130	VP131	VP132	VP133	VP134	VP135	VP136	VP137	VP138	VP139	VP140	VP141	VP142	VP143	VP144	VP145
Bottom	1 (out)	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26 (in)
Sample	VP94	VP95	VP96	VP97	VP98	VP99	VP100	VP101	VP102	VP103	VP104	VP105	VP106	VP107	VP108	VP109	VP110	VP111	VP112	VP113	VP114	VP115	VP116	VP117	VP118	VP119

CONDITIONS?

Sulphidation is EVIDENCE that Required CONDITIONS to create Sulphidation are present.

But Conditions are Governed by Design i.e. are defined by the Manufacturer

LOCATION of the FAILURE ?

A ***LOCAL WEAKNESS*** in the SOLID dielectric insulation in combination with high electrical stress i.e. the

CELLULOSE DI-ELECTRIC STRENGTH COLLAPSE

DEFINITIONS

- **INHIBITOR**: a substance capable of stopping or retarding a chemical reaction.

  Consequently the reaction will be retarded or stopped as long as the inhibitor is present in sufficient concentration.

- **ANTIOXIDANT**: A substance that, when present at a lower concentration than that of the oxidizable substrate, significantly inhibits or delays oxidative processes, while being itself oxidized.

  In primary antioxidants, antioxidative activity is implemented by the donation of an electron or hydrogen atom to a radical derivative.

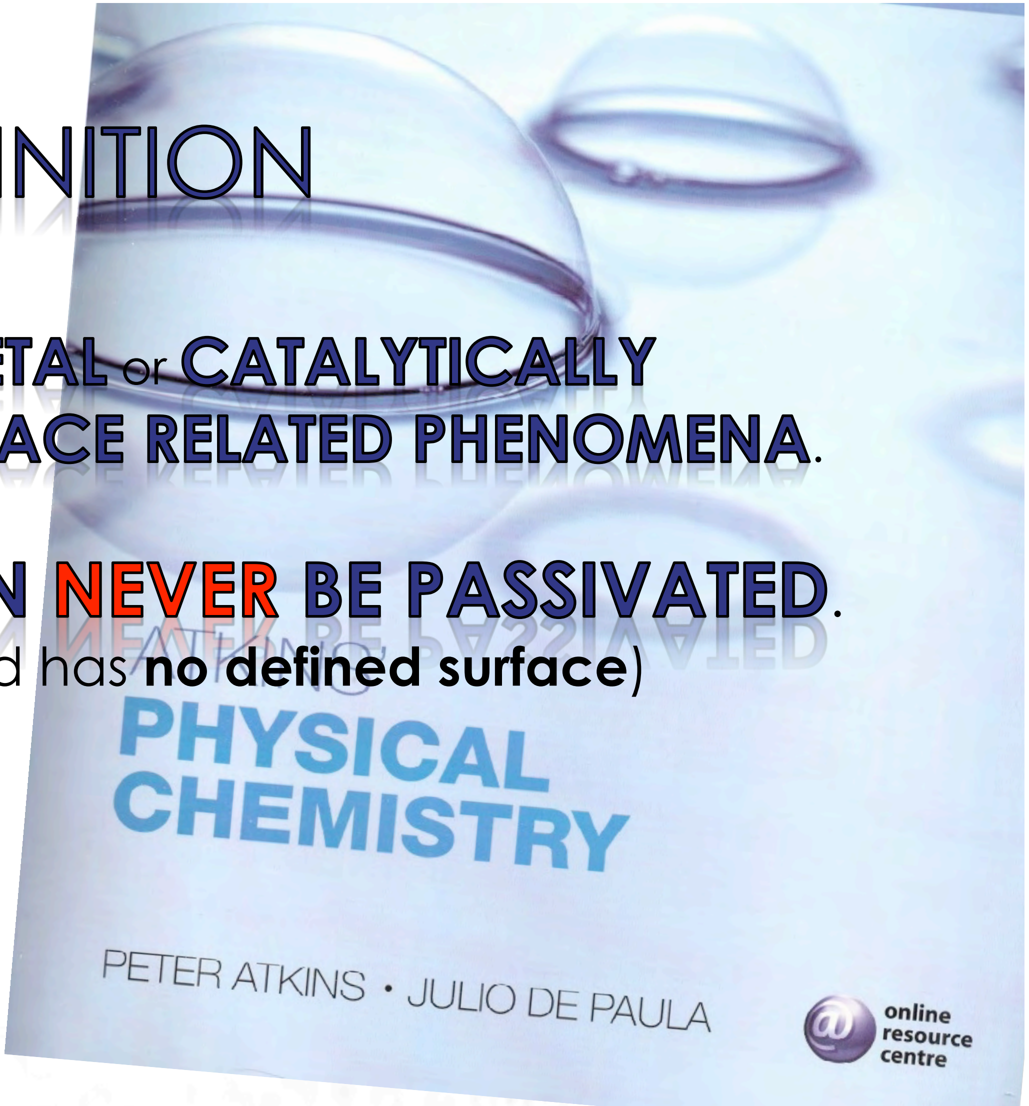
  in secondary antioxidants by the removal of an oxidative catalyst and the consequent prevention of the initiation of oxidation.

- **PASSIVATOR**: definition *NOT found* in Chemistry Dictionaries.

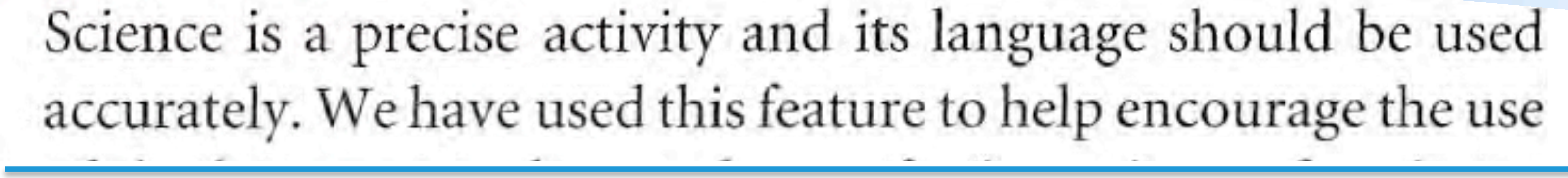
DEFINITION

- **PASSIVATION**: is a **METAL** or **CATALYTICALLY ACTIVE SURFACE SURFACE RELATED PHENOMENA**.

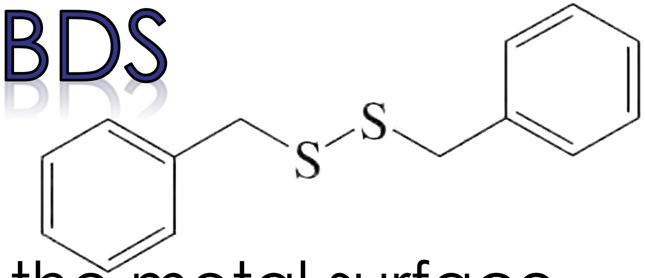
Consequently: an **OIL CAN NEVER BE PASSIVATED**.
(BECAUSE it is **not a metal** and has **no defined surface**)



Notes on good practice


Science is a precise activity and its language should be used accurately. We have used this feature to help encourage the use

THE FUNCTION OF DBDS



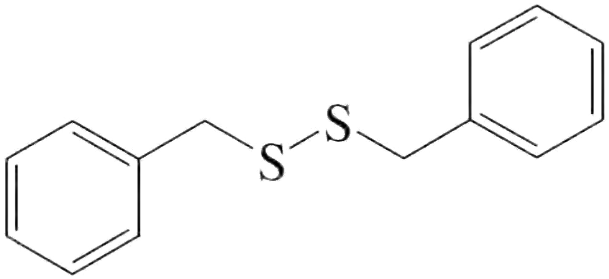
Dibenzyl disulfide

- At low temperatures it ADHERES to the metal surface and passivates it. **REVERSIBLE**!
- At elevated temperatures it REACTS with metal surface and form a sulphide. **IRREVERSIBLE**!

The Surface is Passivated i.e. **DBDS** is a **SECONDARY ANTIOXIDANT** and a **PASSIVATOR**.

- Its HISTORICAL use is to **MANIPULATE** the **OXIDATION STABILITY TEST**.

How Frequent and How Dangerous is DBDS?



Dibenzyl disulfide

- > 13500 transformers tested in Sweden.
- > 75 % contain DBDS.
- DBDS found back to 1965 vintage trx.
- None had failed.

SO WHY IS THERE A PROBLEM?

RESEARCH: DBDS AND BHT, DBDS AND IRGAMET 39

- **DBDS** is an **ANTIOXIDANT** by ***PASSIVATING*** **CATALYTICALLY ACTIVE COPPER SURFACES** such as **COPPER.**
- **BHT** is an **ANTIOXIDANT** by ***REACTING*** with **ORGANIC OXYGEN CONTAINING RADICALS.**
- **BTA** is **BELIEVED** by many **TO BE** a **PASSIVATOR BECAUSE THE WORD PASSIVATOR IS USED** for it.

VP diagnose

RESEARCH PROGRAM REVIEWED BY THIRD PARTY (UNIVERSITY).

SULFIDATION CORROSION INHIBITION

- DBDS corrosion process involves RADICALS.
- BHT radicals react with DBDS radicals.

Why not inhibit DBDS radical reactions by BHT radicals?

RESEARCH REVIEWED BY THIRD PARTY (UNIVERSITY).

PROJECT AIMS & RESEARCH PROGRAM

1. to show that BHT has a positive effect on the rate of copper sulphidation induced by DBDS .

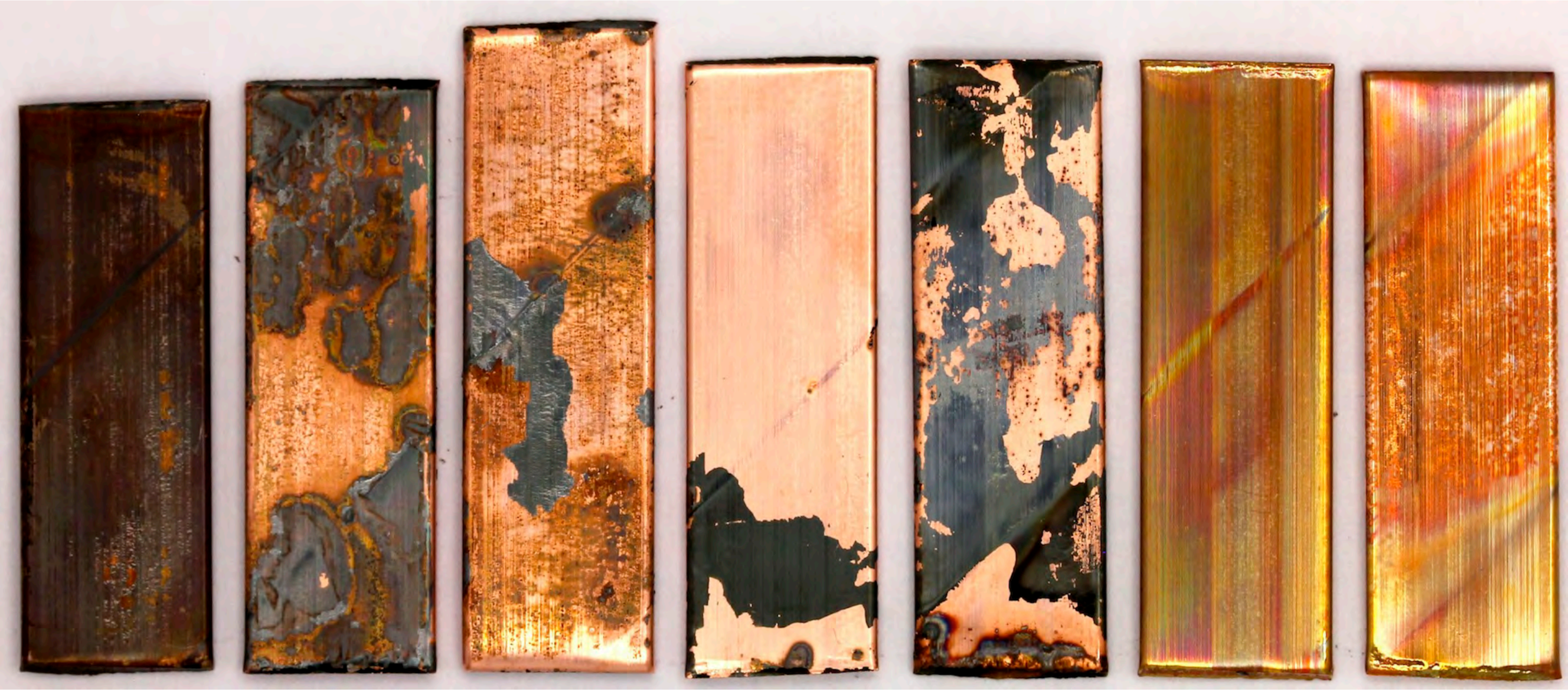
2. To show that BHT has no or very little effect when copper sulphidation is already a fact i.e. imitating the conditions in a real transformer where attack has taken place. i.e. that remedies are not

- BHT & DBDS concentration in oil.
- Copper & Sulphur Concentration in oil and in cellulose.
- Scanning Electron Microscope inspection of selected specimens, both cellulose and conductor.
- Glow Discharge Optical Emission Spectroscopy (GD-OES) for selected.

RESEARCH PROGRAM REVIEWED BY THIRD PARTY (UNIVERSITY).

RESULTS:

- **BHT** inhibits effect of **DBDS** to *some* degree.



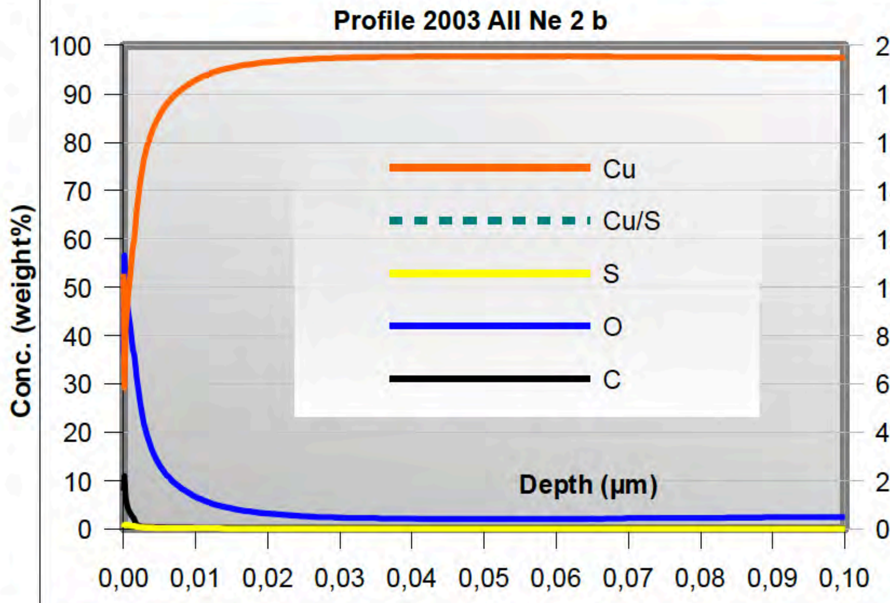
RESEARCH REVIEWED BY THIRD PARTY (UNIVERSITY).

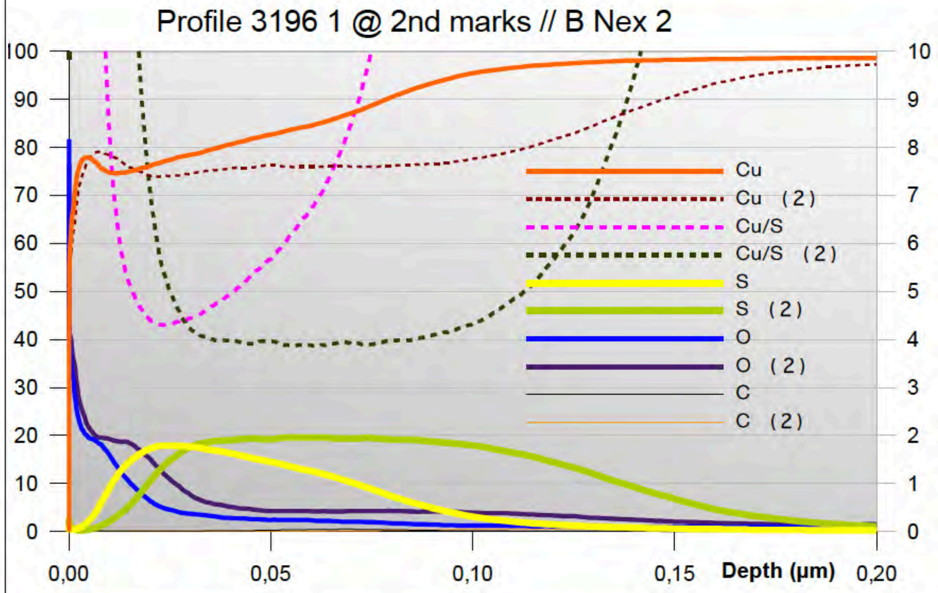
RESULTS:

A

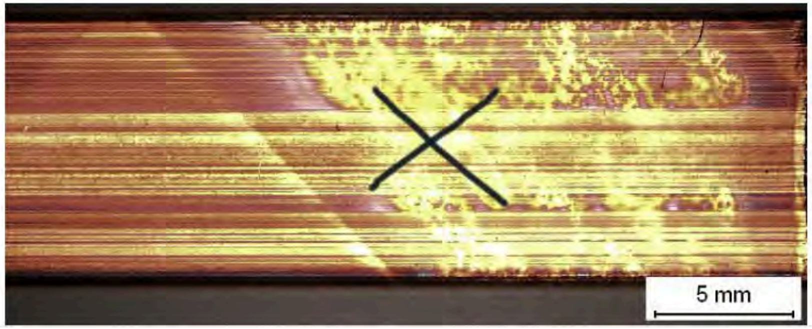
No pre-sulphidation / corrosion ONLY NEXBASE100.

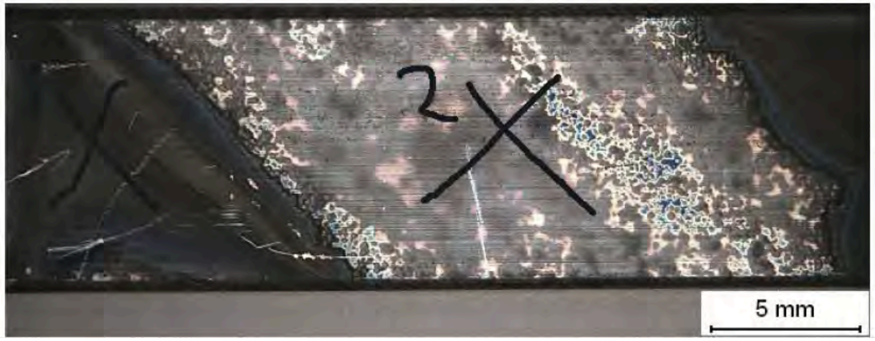
Pre-sulphidation/corrosion 12 days @ 150 C,





All
2 days
(2003)





VP diagnose

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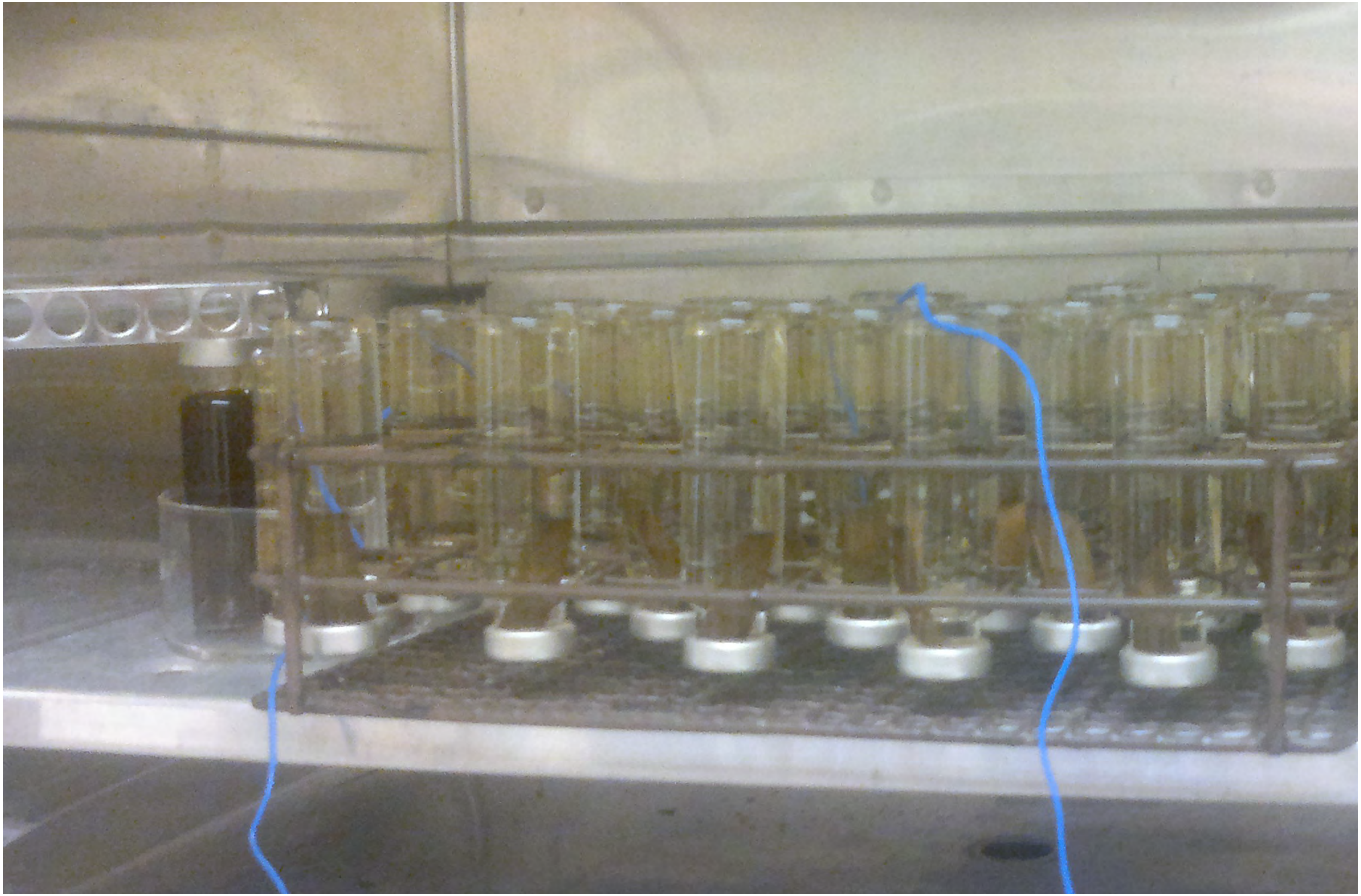

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RESULTS/CONCLUSIONS:

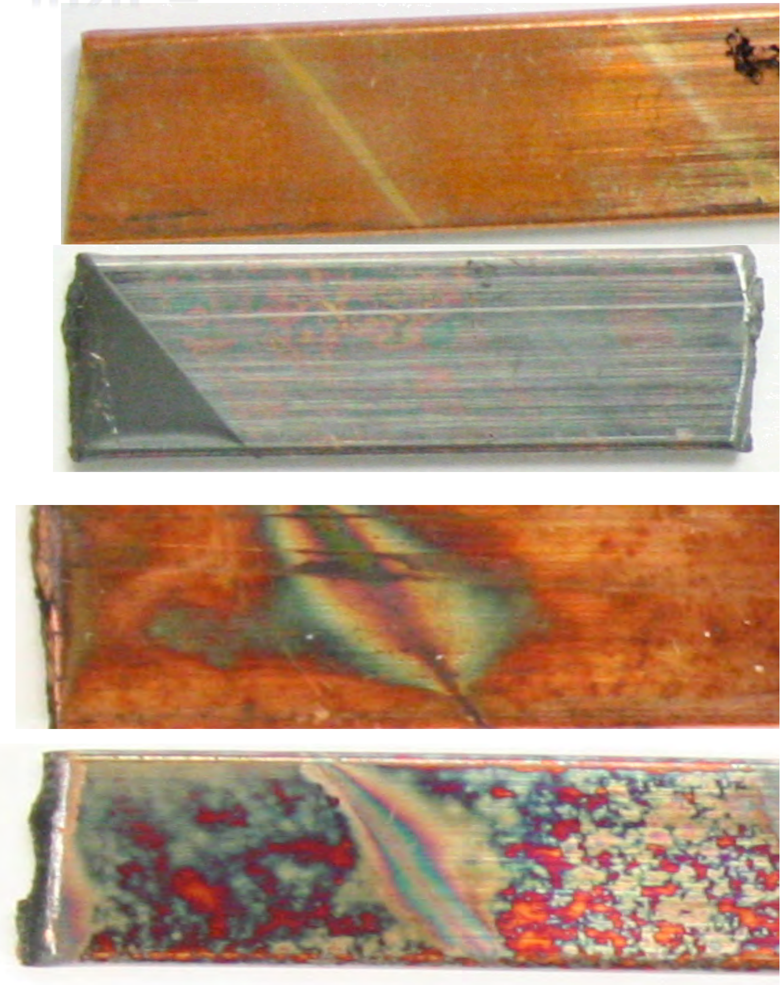
All **TESTING** must be performed in **OXYGEN PRESENCE.**

SEALED VIAL test EXCEEDING 20 min@150 C will present ERRONEOUS RESULTS.

> 99% of all reported research is based on sealed vials/vessels testing i.e. **OXYGEN NOT PRESENT** i.e. **ERRONEOUS TESTING/ RESULTS/CONCLUSIONS/ INTERPRETATION**.

IMPORTANT RESULT: VERIFICATION THAT CCD-TEST IS MISLEADING

(COVERED CONDUCTOR DEPOSITION)



E.g. Chlorine and Phosphorous attack ***have been*** interpreted as Corrosive Sulfur attack.

SULPHIDATION is like every **CHEMICAL PROCESS**:

if conditions are favourable for a process …!!!!!!!!!

Naica,
Chihuahua,
Mexico
lead/silver
mine

500,000
years old
crystals

From: http://channel.nationalgeographic.com/episode/giant-crystal-cave-3569/cave-crystal-giants-1#tab-facts

Do Corrosive Sulfur Remedies exist ?

A ***WEAK*** Design is Always a ***WEAK*** Design.

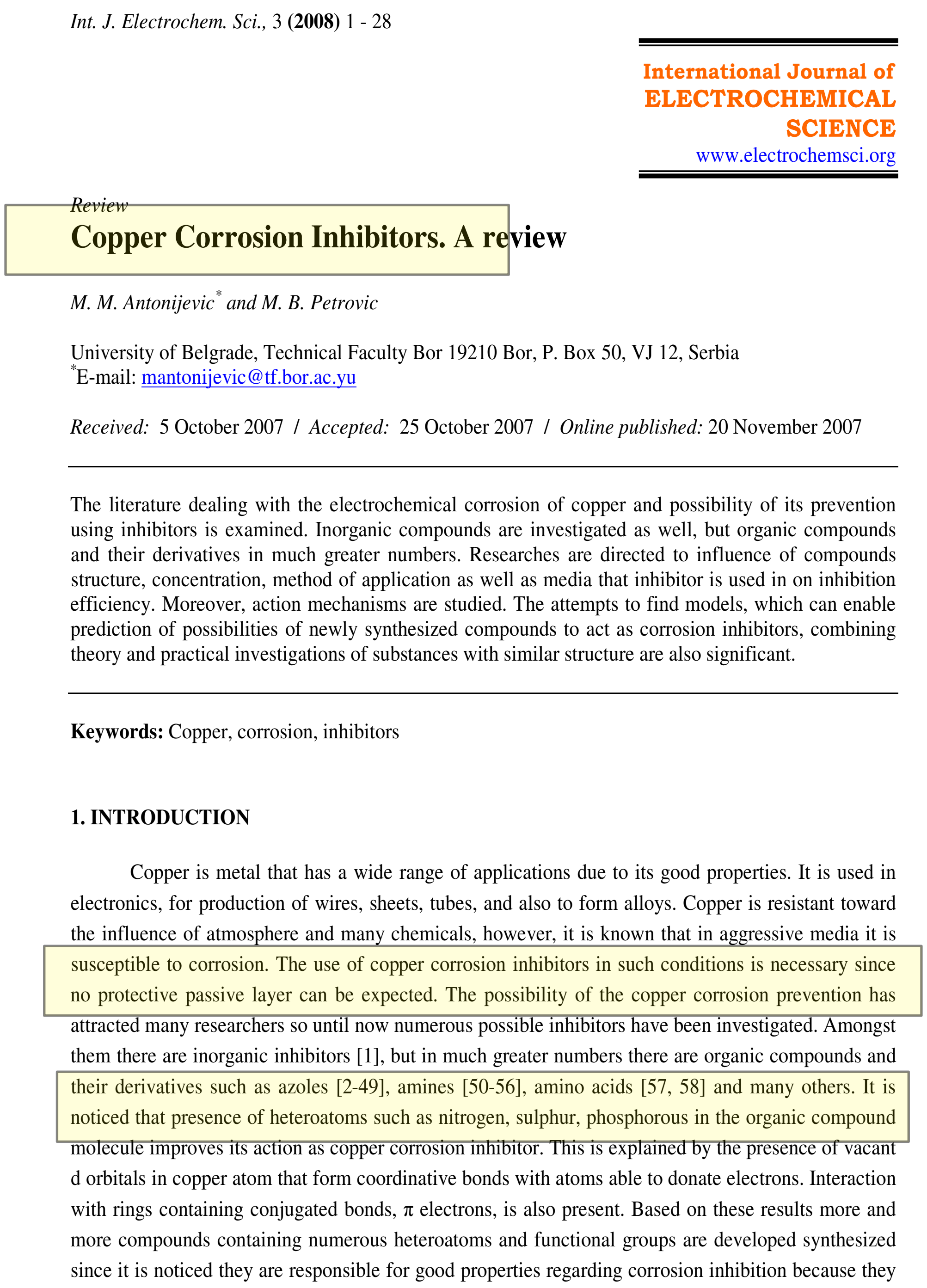
A ***WEAK DESIGN*** + ***BAD OPERATING*** Parameters is a very bad combination.

A ***WEAK DESIGN*** + ***BAD OPERATING*** Parameters + ***DBDS*** in the oil = ***WORST POSSIBLE COMBINATION***.

~~***DE-RATING*** is a the ***ONLY*** possible remedy!~~

Definitions

- **PASSIVATOR**: definition *NOT found* in Chemistry Dictionaries.
- **DEFINITION: RENDERING** a **SUBSTANCE INACTIVE** or **INERT** by **CHEMICAL ACTION.**
- **PASSIVATION** of a **CATALYST** is called ***CATALYST POISONING***.



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Review

Copper Corrosion Inhibitors. A review

M. M. Antonijevic[*] *and M. B. Petrovic*

University of Belgrade, Technical Faculty Bor 19210 Bor, P. Box 50, VJ 12, Serbia
[*]E-mail: mantonijevic@tf.bor.ac.yu

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The literature dealing with the electrochemical corrosion of copper and possibility of its prevention using inhibitors is examined. Inorganic compounds are investigated as well, but organic compounds and their derivatives in much greater numbers. Researches are directed to influence of compounds structure, concentration, method of application as well as media that inhibitor is used in on inhibition efficiency. Moreover, action mechanisms are studied. The attempts to find models, which can enable prediction of possibilities of newly synthesized compounds to act as corrosion inhibitors, combining theory and practical investigations of substances with similar structure are also significant.

Keywords: Copper, corrosion, inhibitors

1. INTRODUCTION

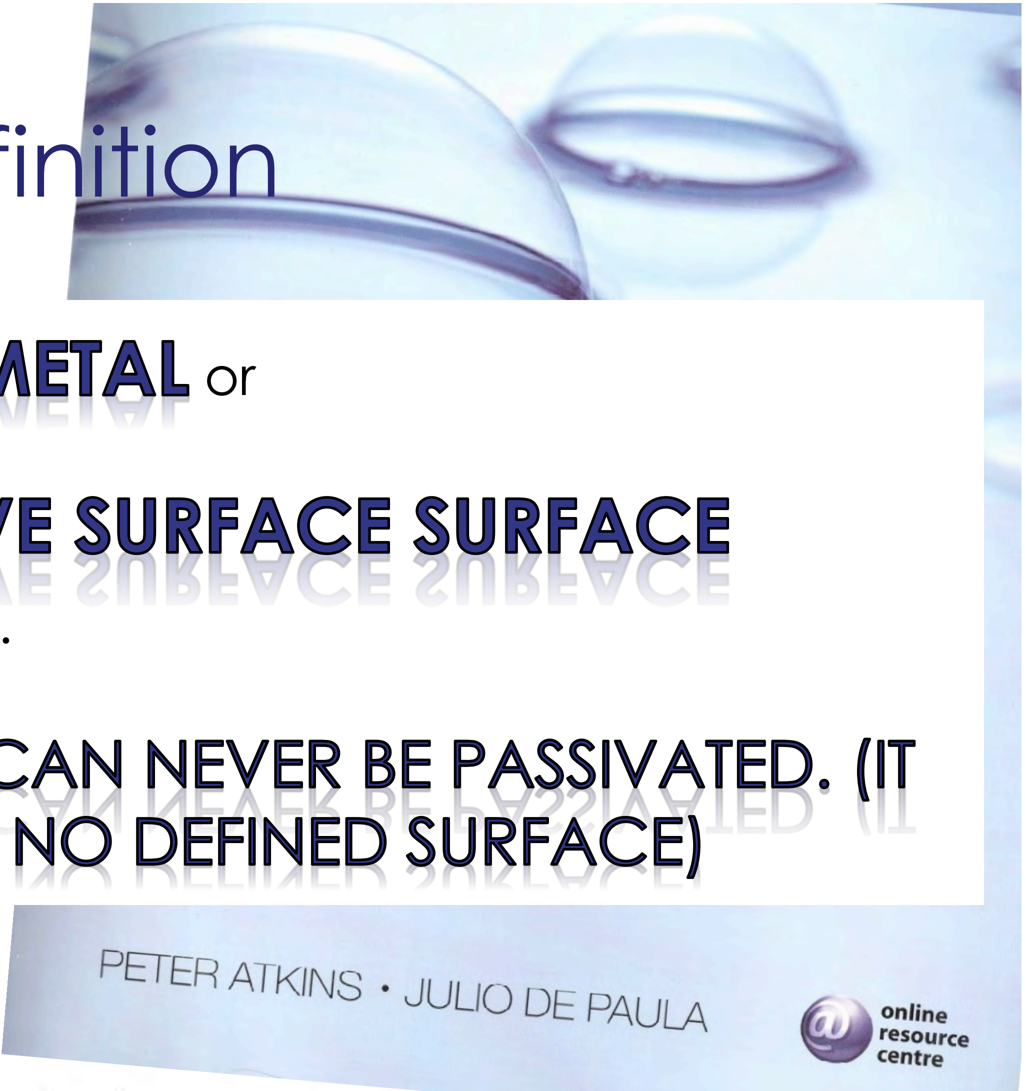
Copper is metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys. Copper is resistant toward the influence of atmosphere and many chemicals, however, it is known that in aggressive media it is susceptible to corrosion. The use of copper corrosion inhibitors in such conditions is necessary since no protective passive layer can be expected. The possibility of the copper corrosion prevention has attracted many researchers so until now numerous possible inhibitors have been investigated. Amongst them there are inorganic inhibitors [1], but in much greater numbers there are organic compounds and their derivatives such as azoles [2-49], amines [50-56], amino acids [57, 58] and many others. It is noticed that presence of heteroatoms such as nitrogen, sulphur, phosphorous in the organic compound molecule improves its action as copper corrosion inhibitor. This is explained by the presence of vacant d orbitals in copper atom that form coordinative bonds with atoms able to donate electrons. Interaction with rings containing conjugated bonds, π electrons, is also present. Based on these results more and more compounds containing numerous heteroatoms and functional groups are developed synthesized since it is noticed they are responsible for good properties regarding corrosion inhibition because they

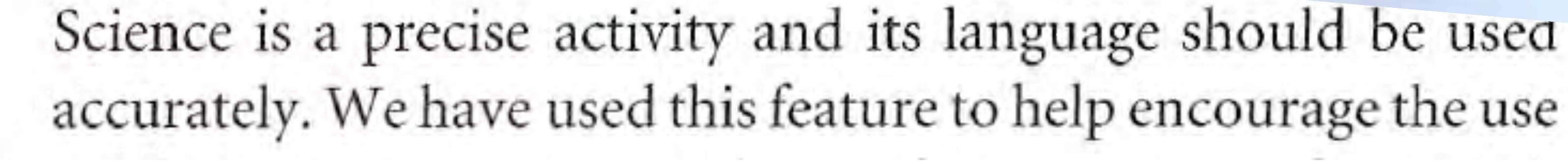
Definition

- **PASSIVATION**: is a **METAL** or

CATALYTICALLY ACTIVE SURFACE SURFACE RELATED PHENOMENA.

CONSEQUENTLY: AN OIL CAN NEVER BE PASSIVATED. (IT IS NOT A METAL AND HAS NO DEFINED SURFACE)





Notes on good practice

Science is a precise activity and its language should be used accurately. We have used this feature to help encourage the use

Copper Pr

- **GASES ADHERE TO METAL**

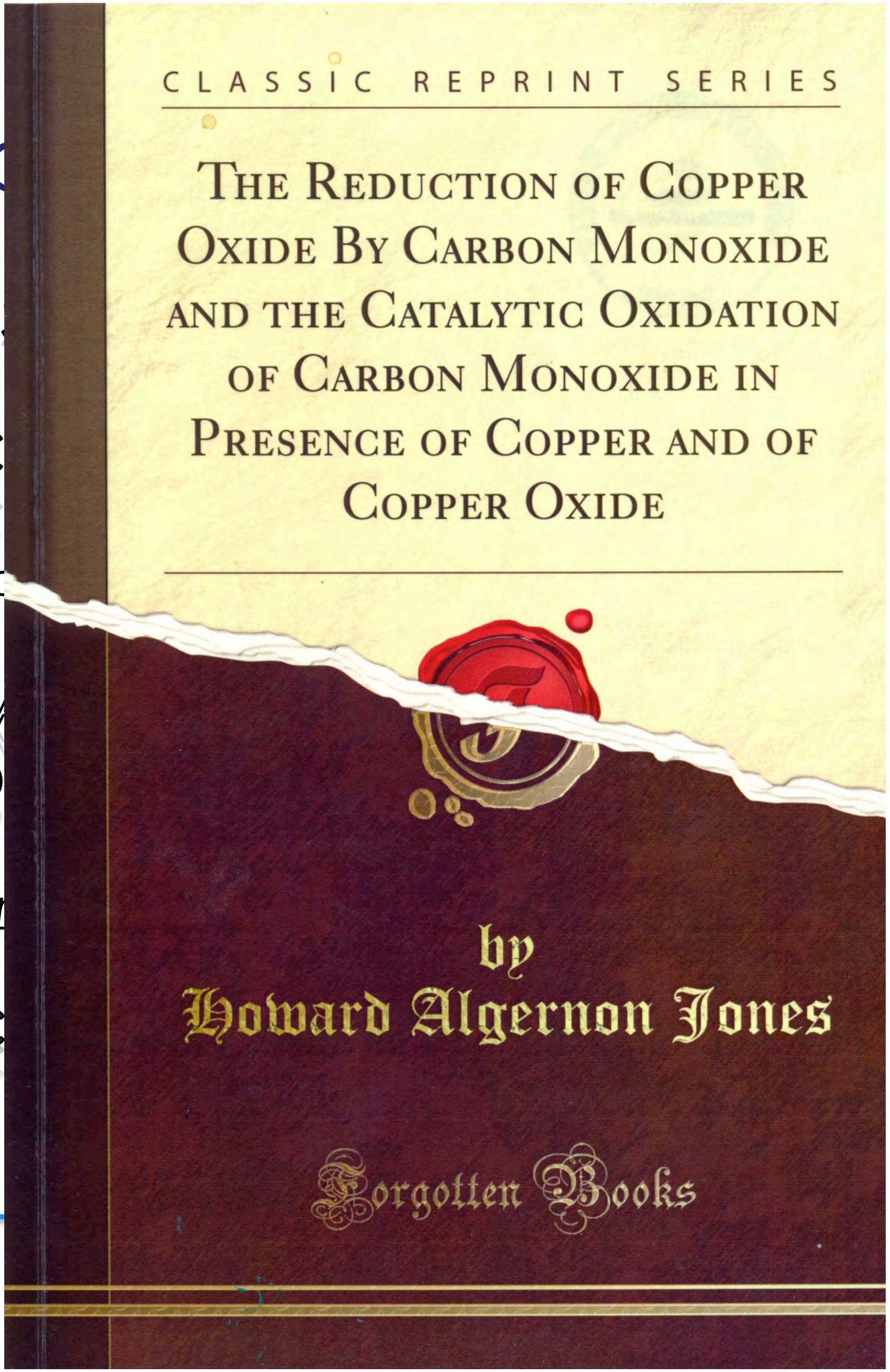
$O_2 > C_2H_2 > C_2H_4 > C$

G.C Bond “Catalysis by Metals” , p

CONSEQUENCE: COPPER W
INDUSTRIAL COMMERCIAL O

Howard Algerno

COPPER IS THE MOST COMMON C
PRODUCTION TODAY.



CLASSIC REPRINT SERIES

THE REDUCTION OF COPPER OXIDE BY CARBON MONOXIDE AND THE CATALYTIC OXIDATION OF CARBON MONOXIDE IN PRESENCE OF COPPER AND OF COPPER OXIDE

by
Howard Algernon Jones

Forgotten Books

Passivation of metals:
BTA project background & scope.

- STATED (BY LA) TO BE IMPOSSIBLE AT GCC-CIGRÉ DUBAI 2007.
- REASON BEING BTA´S STRONG SENSITIVITY TO ELEVATED TEMPERATURE IN OXYGEN PRESENCE I.E. TO OXIDATION.
- HOW TO PROVE NON-FUNCTION WHEN THE INTERNATIONAL METHOD USED TO PROVE ITS FUNCTION IS PROFOUNDLY WRONG? (NO OXYGEN PRESENT).

Method

USE CCD! (FAVOURING STABILITY OF BTA)

USE THE ONLY PARAMETER THAT IMITATES REAL OPERATION! ***TIME***

DECREASE ***TEMPERATURE.***

VP diagnose

RESEARCH REVIEWED BY THIRD PARTY (UNIVERSITY).

Research: BTA and DBDS

- TWO CASES:
  1. PRE-CORRODED (IMITATING ADDITION AFTER LONG TRANSFORMER USE)
  2. BLANK (IMITATING ADDITION AT COMMISSIONING)
- TWO TEMPERATURES (120° & 150° CELSIUS)

RESEARCH REVIEWED BY THIRD PARTY (UNIVERSITY).

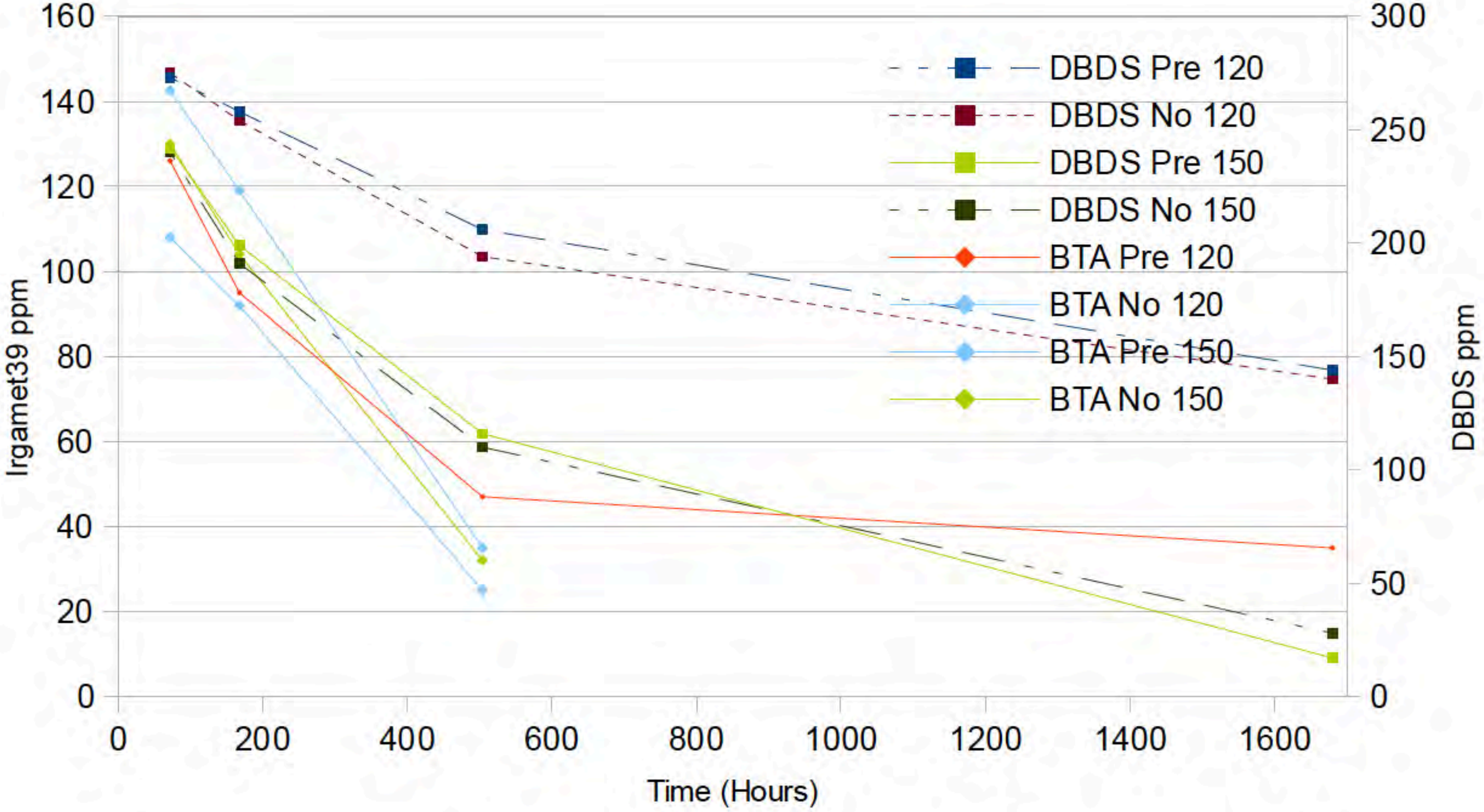
Materials selection

- EXTRUDED (i.e. not drawn) COPPER.
- BASE OIL NEXBASE 7010 i.e. fully saturated stable and NO SULPHUR.
- IRGAMET 39. COMMERCIAL QUALITY.
- DBDS. LAB QUALITY.

VP diagnose

RESEARCH REVIEWED BY THIRD PARTY (UNIVERSITY).

$\delta(BTA)/\delta t > \delta(DBDS)/\delta t$



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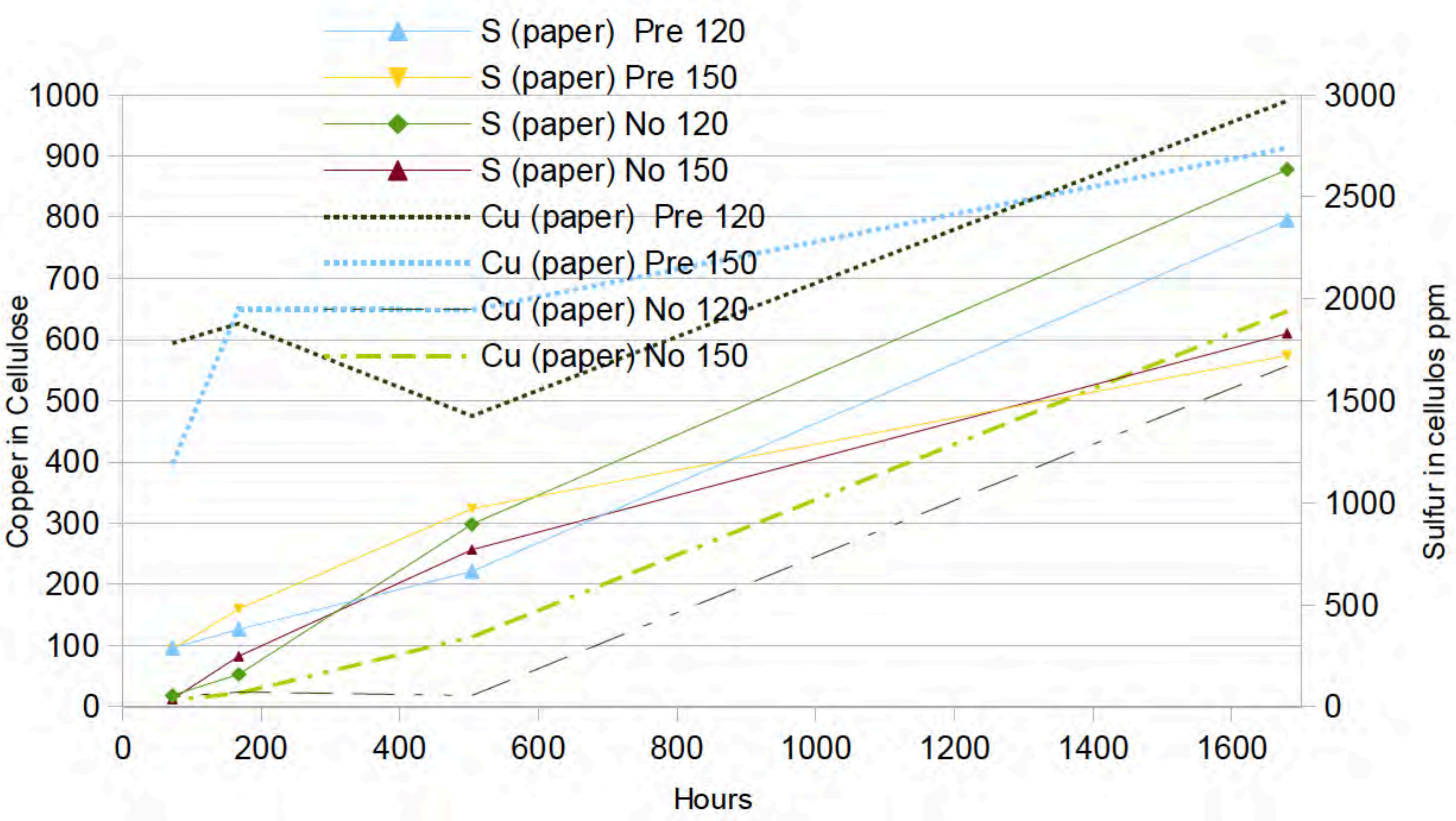
Copper and sulphur in cellulose trends



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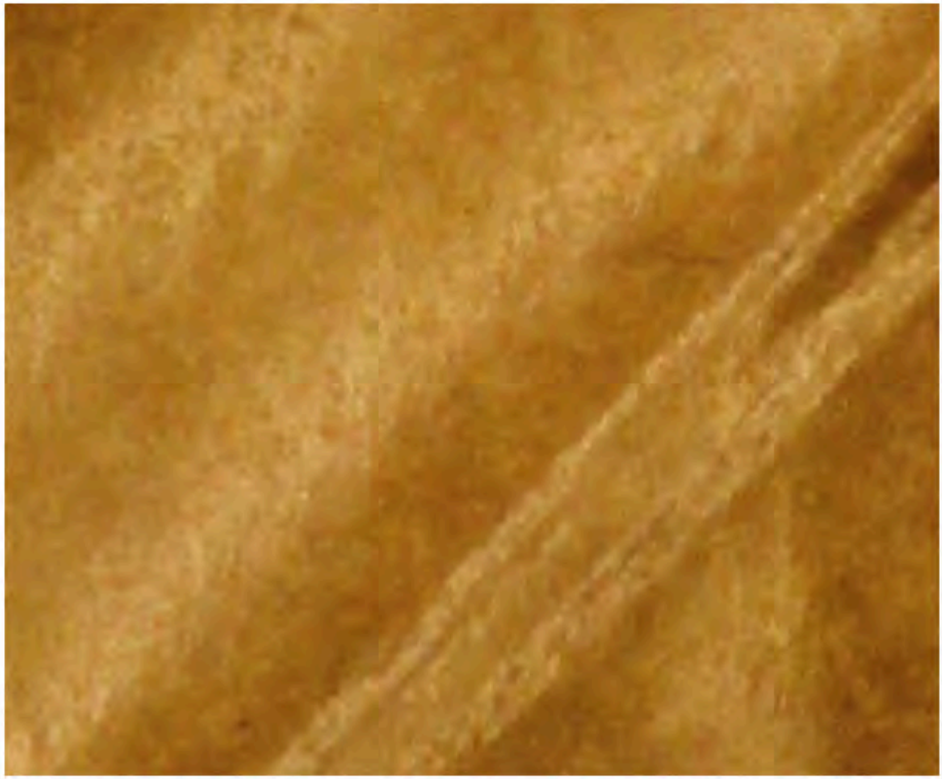
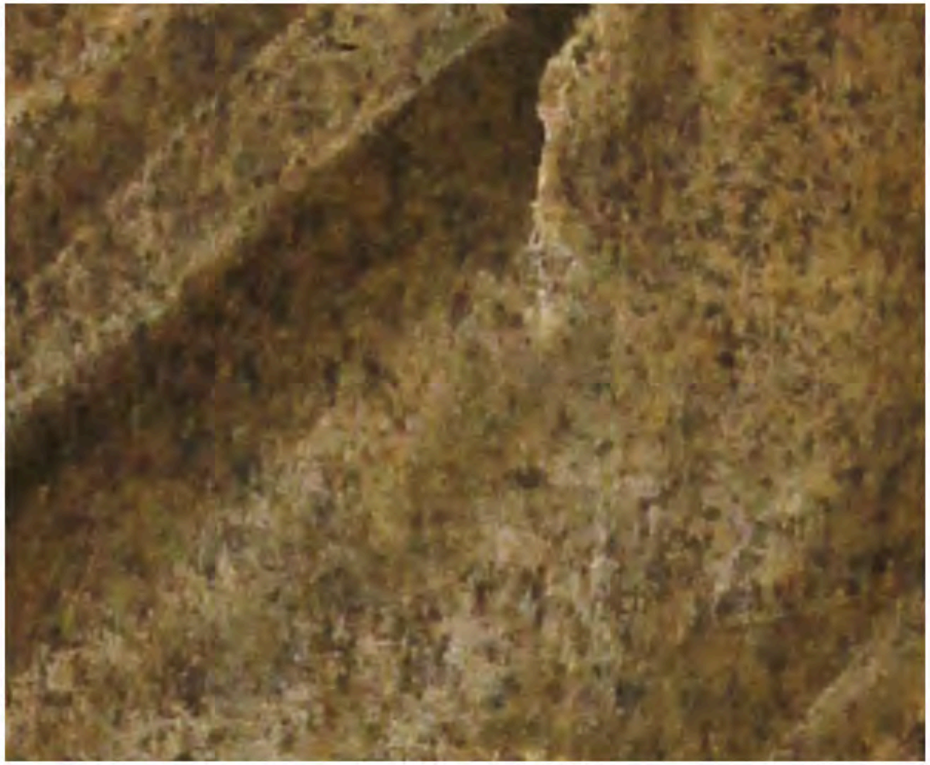
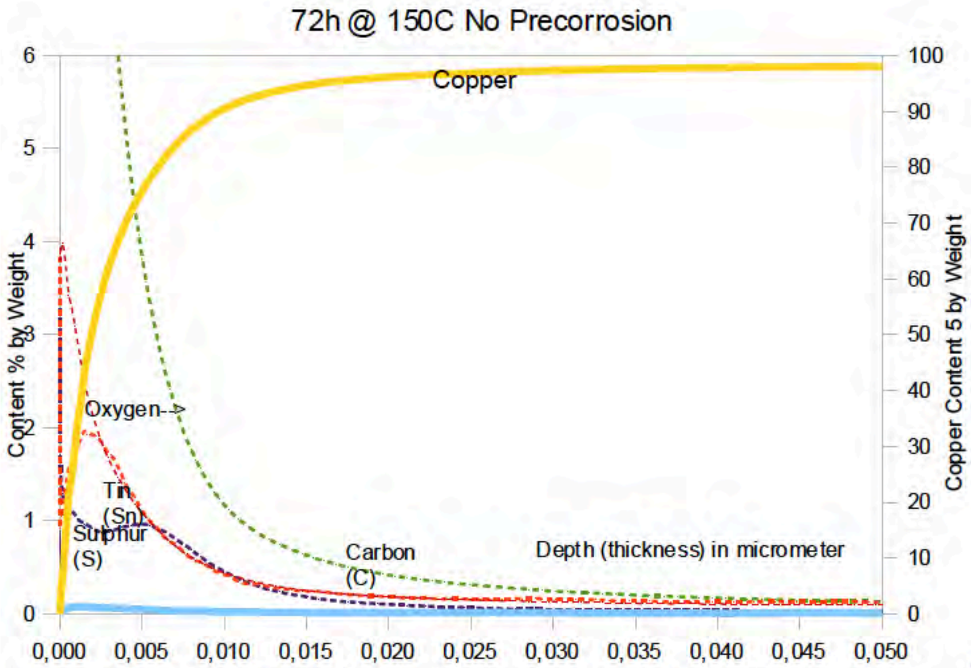
Visual inspection:

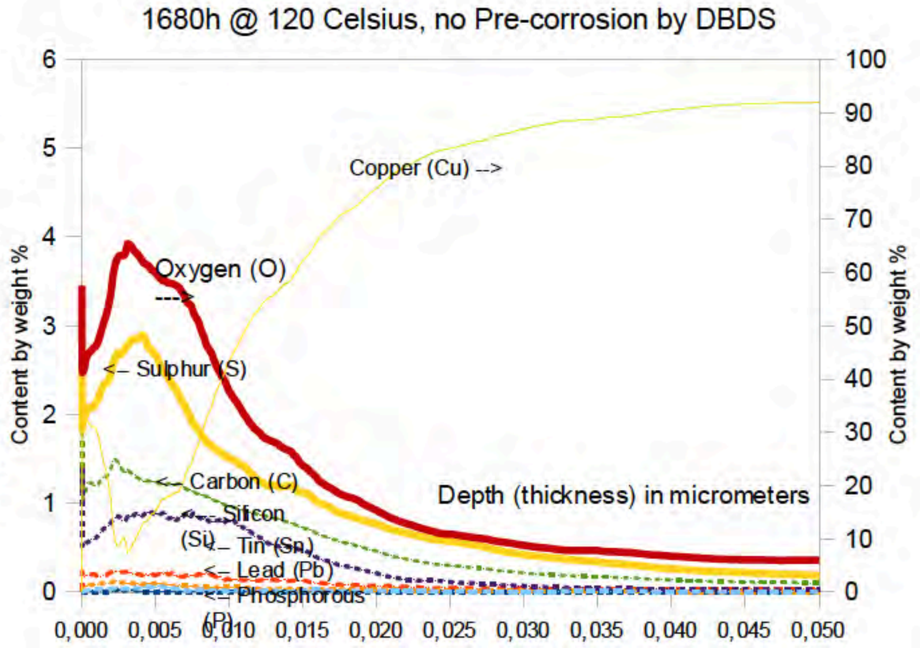
	
Cellulose sample @ 72h 120º ° Celsius and no pre-corrosion. Vague ”stains” can be observed	Cellulose sample @ 1680h 120º ° Celsius and no pre-corrosion. Clear ”stains” are observed

Glow discharge optical emission spectroscopy GD-OES



72h @ 150C No Precorrosion

After 72 hours at 150 ° Celsius an appreciable concentration of TIN and elevated level of LEAD is found close to the surface.'Apart from that the expected elements oxygen, sulphur and copper are found. The protective oxide layer remains intact but sulphur is increasing.



1680h @ 120 Celsius, no Pre-corrosion by DBDS

After 10 weeks TIN has decreased substantially and the general appearance of the graphs has altered completely despite this is compared to a specimen that had been exposed to reaction condition for short time but more severe. This indicates that long term changes are to be expected despite low temperature.

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TWO Hypotheses verified.

- **THE HYPOTHESIS THAT CLASSICAL CHEMISTRY IS STILL CORRECT WAS VERIFIED BY THIS PROJECT.**
- BTA AND ITS DERIVATIVES ARE NOT COPPER PASSIVATORS AND CONSEQUENTLY DOES NOT FUNCTION IN TRANSFORMERS.

Instead BTA is a COPPER CORROSION INHIBITOR as stated by the COPPER PRODUCTION INDUSTRY.

VP diagnose

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Thank You for Your Attention.

IF YOU HAVE ANY QUESTIONS PLEASE SPEAK VERY LOAD AND CLEAR!